International Standard 7693

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Ferrotungsten — Determination of tungsten content — Cinchonine gravimetric method

Ferro-tungstène — Dosage du tungstène — Méthode gravimétrique à la cinchonine

First edition — 1984-03-01

UDC 669.15'27-198 : 543.21 : 546.78 **Ref. No. ISO 7693-1984 (E)**

Descriptors : ferroalloys, ferrotungsten, chemical analysis, determination of content, tungsten, gravimetric analysis.

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been authorized has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 7693 was developed by Technical Committee ISO/TC 132, *Ferroalloys*, and was circulated to the member bodies in April 1982.

It has been approved by the member bodies of the following countries:

Austria	Iran	Romania
Brazil	Italy	South Africa, Rep. of
Canada	Japan	Spain
China	Korea, Rep. of	Sweden
Czechoslovakia	Mexico	United Kingdom
Egypt, Arab Rep. of	Norway	USA
India	Poland	USSR

The member bodies of the following countries expressed disapproval of the document on technical grounds:

Australia
France

Printed in Switzerland

Ferrotungsten — Determination of tungsten content — Cinchonine gravimetric method

1 Scope and field of application

This International Standard specifies a cinchonine gravimetric method for the determination of the tungsten content of ferrotungsten. It also specifies, in the annex, a spectrometric method for the determination of molybdenum which interferes with the determination.

The method is applicable to ferrotungsten having tungsten contents between 70 and 90 % (*m/m*).

2 Reference

ISO 3713, *Ferroalloys — Sampling and preparation of samples — General rules.* [1)]

3 Principle

Dissolution of a test portion using hydrofluoric, nitric and sulphuric acids. Evaporation of the solution until copious white fumes are evolved.

Separation and fusion of the residue with sodium carbonate and diboron trioxide. Dissolution of the fused residue in hot water.

Precipitation of the tungsten with cinchonine and α-benzoin oxime, ignition of the precipitate and weighing of the impure tungstic oxide. Purification of the impure tungstic oxide by fusion with sodium carbonate, dissolution in hot water, filtration and recovery of the insoluble impurities.

Spectrometric determination of molybdenum (see the annex).

Determination of the tungsten content from the difference between the mass of the impure tungstic oxide and that of the impurities.

4 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Sodium carbonate.

4.2 Acetone.

4.3 Diammonium hydrogen citrate [$(NH_4)_2HC_6H_5O_7$].

4.4 Diboron trioxide (B_2O_3).

4.5 Nitric acid, ϱ 1,40 g/ml, approximately 14 mol/l solution.

4.6 Hydrofluoric acid, ϱ 1,16 g/ml, approximately 48 % (*m/m*) solution.

4.7 Hydrochloric acid, ϱ 1,19 g/ml, approximately 12 mol/l solution.

4.8 Ethanol, ϱ approximately 0,790 g/ml.

4.9 Sulphuric acid, diluted 1 + 1.

Carefully add 1 volume of sulphuric acid (ϱ 1,84 g/ml, approximately 18 mol/l solution) to 1 volume of water and mix thoroughly whilst cooling.

4.10 Hydrochloric acid, diluted 1 + 9.

Add 1 volume of the hydrochloric acid (4.7) to 9 volumes of water and mix thoroughly.

4.11 Hydrochloric acid, diluted 1 + 99.

Add 1 volume of the hydrochloric acid (4.7) to 99 volumes of water and mix thoroughly.

4.12 Ammonium hydroxide, diluted 1 + 1.

Add 1 volume of ammonium hydroxide (ϱ 0,885 g/ml, approximately 32 % (*m/m*) solution) to 1 volume of water and mix thoroughly.

1) At present at the stage of draft.

4.13 Ammonium chloride, 20 g/l solution.

Dissolve 2 g of ammonium chloride in water, dilute to 100 ml and mix thoroughly.

4.14 Cinchonine, 125 g/l solution.

Dissolve 125 g of cinchonine in hydrochloric acid (4.7) diluted 1 + 1, and complete to 1 000 ml with that acid.

4.15 α-benzoin oxime, 30 g/l solution.

Dissolve 3 g of α-benzoin oxime in 95 ml of acetone (4.2). Transfer to a 100 ml one-mark volumetric flask, dilute to the mark with water and mix thoroughly.

4.16 Cinchonine/α-benzoin oxime, wash solution.

Place 10 ml of the cinchonine solution (4.14), 5 ml of the α-benzoin oxime solution (4.15) and 2,5 ml of the hydrochloric acid (4.7) in a 1000 ml one-mark volumetric flask, dilute to the mark with water and mix thoroughly.

4.17 Ammonium thiocyanate, 100 g/l solution.

Dissolve 100 g of ammonium thiocyanate in water, dilute to 1000 ml and mix thoroughly.

4.18 Tin (II) chloride, 200 g/l solution in hydrochloric acid (4.7) diluted 1 + 1.

Dissolve 40 g of tin (II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$) in 150 ml of hydrochloric acid (4.7) diluted 1 + 1. Heat gently, cool, dilute to 200 ml with more of the hydrochloric acid diluted 1 + 1 and mix thoroughly.

Prepare this solution immediately before use.

4.19 Phenolphthalein, 1 g/l solution in the ethanol (4.8) solution.

5 Apparatus

Usual laboratory equipment and in particular.

5.1 Spectrophotometer[1], with selector for continuous variation of wavelength, or

5.2 Spectrometer[1], with selector for discontinuous variation of wavelength, equipped with appropriate filters giving maximum transmission at a wavelength of 460 nm.

5.3 Cells[1], of thickness 1 (or 2) cm.

6 Sample

Use powder which will pass through a sieve of aperture size 160 µm, prepared in accordance with ISO 3713.

7 Procedure

7.1 Test portion

Take a test portion of 1 ± 0,001 g.

7.2 Blank test

Carry out a blank test in parallel with the determination, following the same procedure and using the same quantities of all the reagents, but omitting the test portion.

7.3 Control test

Check the validity of the operating procedures used by carrying out, in parallel with the determination and following the same procedure, determination(s) of the tungsten content(s) of one or several samples of the same type, having known tungsten content(s).

7.4 Determination

7.4.1 Dissolution

Place the test portion in a 60 ml platinum crucible fitted with a platinum lid and add 5 ml of the hydrofluoric acid (4.6). Add the nitric acid (4.5) carefully, drop by drop, and heat to light boiling until decomposition of the test portion is complete.

Remove from the source of heat and rinse the sides of the crucible and the lid with water. Add 15 ml of the sulphuric acid solution (4.9) and heat carefully on a sand-bath until copious white fumes are evolved.

Allow to cool, and then dissolve the soluble salts in 10 ml of the hydrochloric acid (4.7) and 30 ml of hot water.

7.4.2 Filtration of impure tungstic oxide

Filter the contents of the 60 ml platinum crucible on a fine-grained ashless filter paper, collecting the filtrate in a 600 ml beaker. Wash the filter and the precipitate with the hydrochloric acid solution (4.10).

Dissolve the precipitate (essentially tungstic acid) in the smallest possible quantity of ammonium hydroxide solution (4.12), then wash the filter with the ammonium chloride solution (4.13). Collect the solution resulting from dissolution and washing with the filtrate in the 600 ml beaker.

7.4.3 Treatment of any insoluble residue remaining on the filter

Transfer the filter with any insoluble residue to the original 60 ml platinum crucible. Dry and ignite the filter, heating the residue at a temperature below 750 °C. Cool, add 0,5 g of the sodium carbonate (4.1) and 0,5 g of the diboron trioxide (4.4). Heat over a burner, gently at first, and then more strongly, until the mixture just fuses. Cool, and then dissolve the fused material in hot water. Filter the solution obtained on a fine-

1) These are required for the determination of molybdenum (see the annex) when the molybdenum content of the sample is not known.

grained filter paper, collecting the filtrate in the same 600 ml beaker (see 7.4.2). Wash the filter with hot water.

7.4.4 Precipitation of tungsten

7.4.4.1 Acidify the solution in the 600 ml beaker by adding 10 ml in excess of the hydrochloric acid (4.7). Boil for 5 min. Remove the beaker from the source of heat and dilute the contents to approximately 450 ml with hot water. Add 30 ml of the cinchonine solution (4.14) and a small amount of ashless filter paper pulp, and allow the solution to stand for 30 min at 90 °C, agitating it from time to time. Then allow the solution to stand at ambient temperature for at least 4 h or, preferably, overnight.

7.4.4.2 Add 5 ml of the α-benzoin oxime solution (4.15) and agitate vigorously for a few minutes. Allow to stand for 1 h at ambient temperature. Filter using a conical filter funnel with an 11 cm diameter filter paper containing a little ashless filter paper pulp.

Wash three times by decantation, then with the hot cinchonine/α-benzoin oxime solution (4.16) and then several times with cold hydrochloric acid solution (4.11). Finally wash with cold water.

Transfer the filter containing the precipitate to a tared platinum crucible and heat carefully to complete incineration. Add a few drops of the nitric acid (4.5) and evaporate to dryness on a sand-bath. Ignite the tungstic oxide (for approximately 30 min) at a temperature not exceeding 750 °C[1] in an electric muffle furnace until constant mass is attained.

Allow to cool in a desiccator and weigh the crucible containing the impure tungstic oxide.

7.4.4.3 Add 5 g of the sodium carbonate (4.1) and mix completely with the impure tungstic oxide. Cover the mixture with 1 to 2 g of the sodium carbonate (4.1) and heat the mixture until it fuses.

Swirl the crucible to detach the tungstic oxide adhering to the walls of the crucible to incorporate it with the fused mass. Cool, and dissolve the fused material in hot water. Add some drops of the ethanol (4.8), heat for a few minutes, filter and wash the crucible and residue with hot water, retaining the filtrate (filtrate A). Transfer the filter containing the residue to the crucible and ignite; add 1 to 2 g of the sodium carbonate (4.11) and again fuse.

Dissolve the fused mass in water, add some drops of the ethanol (4.8), filter and wash the residue thoroughly to remove the sodium carbonate completely (filtrate B). Combine filtrate A with filtrate B in order to determine the molybdenum content (see the annex) if required.

Place the filter containing the residue in the crucible, ignite, at a temperature not exceeding 750 °C in the electric muffle furnace. Allow to cool and weigh.

8 Expression of results

The tungsten content, expressed as percentage by mass, is given by the formula

$$\frac{0{,}793\,0\,[(m_1 - m_2) - (m_3 - m_4)]}{m_0} \times 100$$

where

m_0 is the mass, in grams, of the test portion;

m_1 is the mass in grams, of the impure tungstic oxide (see 7.4.4.2);

m_2 is the mass, in grams, of the residue obtained after fusion with sodium carbonate (see 7.4.4.3);

m_3 is the mass, in grams, of the impure tungstic oxide in the blank test (see 7.2);

m_4 is the mass, in grams, of the residue obtained after fusion with sodium carbonate in the blank test (see 7.2);

0,793 0 is the conversion factor to express the tungstic oxide content as the tungsten content.

9 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) identification of the sample;

c) the result and the method of expression used;

d) any unusual features noted during the determination;

e) details of any operations not specified in this International Standard or regarded as optional.

1) The temperature of 750 °C should not be exceeded, because, at a temperature even slightly higher than this, tungstic oxide volatilizes slowly and continuously and this may lead to appreciable errors.

Annex

Determination of molybdenum

A.1 General

The tungstic oxide obtained may contain traces (some hundredths of 1 %) of molybdenum in the form of molybdic oxide. If the molybdenum content is not known, it is necessary to determine it spectrometrically and to correct the mass of tungstic oxide.

A.2 Procedure

Boil the combined filtrate (A + B) to concentrate the solution to a volume of approximately 80 ml. Transfer the solution to a 100 ml one-mark volumetric flask, dilute to the mark with water and mix thoroughly.

Transfer a 10 ml aliquot portion of this solution, containing not more than 0,30 mg of molybdenum, to a 50 ml one-mark volumetric flask. Add 2 g of the diammonium hydrogen citrate (4.3) and agitate until dissolution is complete. Add 3 drops of the phenolphthalein solution (4.19), the hydrochloric acid (4.7) until the red coloration is eliminated, and then 5 ml of the hydrochloric acid in excess. Add, agitating after each addition, 5 ml of the ammonium thiocyanate solution (4.17), 20 ml of the acetone (4.2) and 7 ml of the tin (II) chloride solution (4.18). Dilute to the mark with acetone and mix thoroughly.

Carry out the spectrometric measurements on the solution, using the spectrometer (5.1) set a wavelength of approximately 460 nm, or the spectrometer (5.2) equipped with the appropriate filters. (Cells of thickness 1 cm are generally used.)

Carry out the measurements within a period not exceeding 15 min after coloration. Determine the molybdenum content from the calibration graph and (see clause A.3) and subtract the mass of molybdic oxide thus obtained from the mass of the impure tungstic oxide.

A.3 Preparation of the calibration graph

Prepare standard matching solutions by placing varying amounts of standard molybdenum solutions (corresponding to 0,050 mg and 0,010 mg of Mo per litre) into a series of six 50 ml one-mark volumetric flasks. Add to the contents of each flask 2 g of the diammonium hydrogen citrate (4.3) and agitate until dissolution is complete. Proceed as described in clause A.2, second paragraph, from "Add 3 drops of the phenolphthalein solution (4.19)...".

Plot a graph having, for example, the measured absorbances as ordinates and the corresponding molybdenum contents as abscissae.